Electrochemical Properties of AB₅ Type Flaky Hydrogen Storage Alloy Powders Prepared by Two-Stage Rapid Quenching

Yang CUI*, Tetsu YAMAMOTO*, Masahiro OGUCHI**,
Yoshio HAKAKAWA** and Seiji KAMASAKI*

*Graduate School of Engineering, Tokyo Metropolitan University (1-1, Minami-ohsawa, Hachioji-shi, Tokyo 192-0397)

**Teikoku Piston Ring Co., Ltd. (2-1-13, Shinmei-cho, Okaya-shi, Nagano 394-8511)

AB₅ type LaNi_{3.5}Co_{1.1-x}Cr_xAl_{0.4} (x=0, 0.1) alloy powders were prepared by two-stage rapid quenching as negative electrode materials for Ni-MH batteries. The crystal structures, morphologies and electrochemical properties were examined. The results of X-ray diffraction analysis showed that both of these alloys had a typical hexagonal CaCu₅-type crystal structure. In recovered powders, a small quantity of the powders with uneven form were mixed with the flaky form powders that we have intended. The charge-discharge cyclic stability and discharge rate performance of chromium-containing LaNi_{3.5}Co_{1.0}Cr_{0.1}Al_{0.4} alloy electrodes were much better than those of chromium-free LaNi_{3.5}Co_{1.1}Al_{0.4} alloy electrodes. Additionally, we examined the arranged packing effect of the flaky powders in the disc electrodes on the discharge rate performance. We confirmed that the performance could be improved by the arranged packing technique.

Key Words : Two-Stage Rapid Quenching, Hydrogen Storage Alloy, AB₅ Type Flaky Powder, Ni-MH Battery, Arranged Packing Electrode

1. Introduction

In recent years, nickel-metal hydride (Ni-MH) batteries, using AB₅ type hydrogen storage alloys as negative electrode materials, have been widely used for the power sources of hybrid electric vehicles (HEV) and so on because of their excellent features, such as the environmental friendliness and high energy density. The development of more and more high-functional hydrogen storage alloy electrodes, having high power density and good charge-discharge rate performance, must enable us to enjoy a more comfortable long distance drive.

LaNi₅ as the parent compound of AB₅ type alloys has some peculiar problems of strong corrosion sensitivity to alkaline electrolyte, low electrochemical activity and so on¹⁾. On focusing to alloy composition, metallurgical structure and surface modification, so many investigations have ever been made to improve the alloy performance^{2)~17)}. It was clarified that the partial substitution of nickel by cobalt and aluminum resulted in a prominent increase of the cyclic durability^{1),6)~9),12),17)}. In our original standpoint, we proceeded the analyses of the alloy surface alteration process in strong alkaline electrolyte and the role of the alloy constituent elements in this process. Consequently, we proposed originally designed LaNi_{3.5}Co_{1.1}Al_{0.4} alloy with extremely high charge-discharge cyclic retention as anode of Ni-MH battery¹⁶⁾. On the other hand, Sakai et al. found that the rapidly quenched alloys with the columnar structure had excellent activity and cyclic durability compared to those of the arc

melted alloys^{7)~11)}.

In this study, we prepared thin flaky LaNi_{3.5}Co_{1.1-x}Cr_xAl_{0.4} (x=0, 0.1) alloy powders by two-stage rapid quenching¹⁸⁾ in order to utilize the features of multi-component and rapidly quenched alloys mentioned above, and evaluated their activation characteristics, cyclic durability and discharge rate performance. Chromium has less positive oxidation-reduction potential and smaller electro-negativity than nickel¹⁹⁾. It is expected that the addition of chromium to alloy improve the cyclic durability and discharge rate performance. Additionally, we examined the arranged packing effect of the flaky powders in the disc electrodes on discharge rate performance.

2. Experimental

The mother alloys of LaNi_{3.5}Co_{1.1-x}Cr_xAl_{0.4} (x=0, 0.1) were synthesized by arc melting from the mixtures of the element metal powders. Figure 1 shows the apparatus for two-stage rapid quenching. The mother alloys were set in the crucible and melted by high frequency induction method. Then they were atomized into spherical liquid droplets by argon gas blowing at dynamic pressure 3.92 MPa as the first rapid quenching. For the second rapid quenching, these droplets were run against the water-cooled and highly rotated spindle-shape rotor with the speed of 5,000 rpm. At this second stage, the spherical droplets were changed the form to thin flakes¹⁸⁾. They were recovered in acetone and sieved in the groups of three sizes, under 90 μm, 90–150 μm and 150–1,000 μm, without exposure to air. A large number of

Fig. 1 Apparatus for two-stage rapid quenching.

Fig. 2 Electrode powder vibrator using diaphragm pump.

spherical powders remained in the group of the size under $90\text{ }\mu\text{m}$. We used, therefore, the other two group powders in this research. We named the samples E4-1 ($90\text{--}150\text{ }\mu\text{m}$) and E4-2 ($150\text{--}1,000\text{ }\mu\text{m}$) for $\text{LaNi}_{3.5}\text{Co}_{1.1}\text{Al}_{0.4}$ alloy, and E5-1 ($90\text{--}150\text{ }\mu\text{m}$) and E5-2 ($150\text{--}1,000\text{ }\mu\text{m}$) for $\text{LaNi}_{3.5}\text{Co}_{1.0}\text{Cr}_{0.1}\text{Al}_{0.4}$ alloy, respectively.

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were used for structural analyses. Disc electrodes of 13 mm in diameter, containing 0.25 g of flaky alloy powder and 0.75 g of copper powder as binder, were made by cold pressing at pressure of 5.2 MPa for electrochemical tests. A vibration technique was used to make the arranged packing electrodes. Figure 2 shows the electrode powder vibrator for arranged packing. A press pot with the mixture of flaky alloy and copper powders was placed on the vibrator. Then the vibrator was operated for 0.5 h so as to arrange the flaky alloys in parallel. The electrochemical properties of the elec-

Fig. 3 SEM images of E5-1 powders (a) and the cross section of the arranged packing electrode of E5-2 powders (b).

Fig. 4 XRD profiles of two-stage quenched E4-1 and E5-1 alloy powders.

trodes were examined in the electrolyte of 6 M KOH with platinum plate as counter electrode and Hg/HgO electrode as reference electrode. The cell was controlled at $25\pm1^\circ\text{C}$. The electrodes were charged for 4 h at 100 A/kg and discharged at $50\text{--}600\text{ A/kg}$ up to the cut off potential of -0.65 V vs. Hg/HgO . The pause of 0.5 h was held between charge and discharge for the rest.

3. Results and discussion

3. 1 Morphology and crystal structure

Figure 3 shows the SEM images of E5-1 powders (a) and the cross section of the arranged packing electrode of E5-2 powders (b). In the recovered powders, a small amount of the powders with uneven form were mixed in the flaky powders. All of the flaky powders had a columnar structure. The aspect ratios of E4-1, E5-1 and E4-2, E5-2 alloys were about 2.7 and 5.5, respectively. The uneven powders were formed on the rotor by heap of atomized droplets.

XRD profiles for E4-1 and E5-1 powders are illustrated in Figure 4 and lattice parameters are summarized in Table 1. All of the alloys synthesized in this research had a typical hexagonal CaCu_5 -type structure. The chromium substitution for cobalt resulted in a small lattice expansion because of the atomic radius difference between chromium (0.1276 nm) and cobalt (0.1253 nm).

3. 2 Activation characteristics and cyclic durability

Figure 5 shows the results of the charge-discharge cycle tests for the random packing electrodes of E4-1 and E5-1 powders without arrangement. Discharge current density was 100 A/kg. Compared with the electrodes of arc-melted powders, those of two-stage quenched powders, directly recovered in acetone without exposure to air, showed good activation characteristics. We could achieve the maximum discharge capacity for the electrode of E4-1 powders to repeat the charge-discharge cycles of only about 10 times, while the cyclic repetitions of about 20 times were necessary for the electrodes of arc-melted chromium-free $\text{LaNi}_{3.5}\text{Co}_{1.1}\text{Al}_{0.4}$ powders¹⁶⁾. However, the addition of chromium to the alloys resulted in the decrease of the activation characteristics. It took

Table 1 Crystallographic data of alloy E4-1 and E5-1.

Alloy	Lattice parameter and cell volume		
	a (nm)	c (nm)	V (nm ³)
E4-1	0.50340	0.40078	0.08795
E5-1	0.50365	0.40246	0.08841

Fig. 5 Charge-discharge cyclic characteristics of the electrodes of two-stage quenched E4-1 and E5-1 alloy powders.

Fig. 6 Discharge rate performance of the electrodes of two-stage quenched alloy powders.

(a) The random packing electrodes of E4-1 and E5-1 alloy powders.

(b) The random packing and the arranged packing electrodes of E5-2 alloy powders.

about 20 cycles for the electrode of chromium-containing rapid quenched powders E5-1 to achieve the maximum capacity.

Although the chromium substitution for cobalt also led to a little decrease of the maximum discharge capacity, the cyclic durability was extremely improved. The degradation of rare earth metal-based alloy electrodes was mainly caused by the deactivation of electrochemical catalyst nickel^{15), 16)}. It could be considered that the substituted chromium, with less positive oxidation-reduction potential than nickel, was preferentially oxidized to nickel in alkaline electrolyte so as to suppress the deactivation of catalyst nickel. The results electrochemically evaluated are listed in Table 2.

3. 3 Discharge rate performance

Figure 6(a) shows the evaluation results of the discharge rate performance on the electrodes of E4-1 and E5-1 powders. We can see that the performance of the electrode of chromium-containing E5-1 powders is much better than that of the electrode of chromium-free E4-1 powders. For example, the retentions of E 5-1 and E4-1 electrode at discharge current density of 400 A/kg are 80% and 67%, respectively.

The discharge rate performance is strongly influenced not only by the activities of the electrode but also by the hydrogen diffusing rates. The activation characteristic of chromium-free electrode was better than that of chromium-containing one (see section 3.1). Therefore, it was suggested that the improvement of discharge rate performance was strongly concerned to the improvement of hydrogen diffusibility in the

Table 2 Characteristics of the electrodes of E4-1 and E5-1 alloy powders.

Alloy	Degradation (Ah/kg/cycle)	$C_{\max}^{*1}$ (Ah/kg)	ΔH_f^{*2} (KJ/mol-H ₂)
E4-1	0.334	288	-38.3
E5-1	0.221	281	-37.8

*1 the maximum discharge capacity

*2 the calculated values of the hydride formation enthalpy

Fig. 7 Scheme of the random packing and the arranged packing electrodes.

alloys.

Hydride formation enthalpies (ΔH_f) of the alloys in this research, calculated from the rest potentials of fully charged electrodes, are listed in Table 2. The entropies were assumed to be constant at $134 \text{ J K}^{-1} \text{ mol H}_2^{-1}$ ²⁰⁾. The addition of chromium revealed the increase of the crystallographic cell volume (see Table 1) and the increase of the hydride formation enthalpy (see Table 2) of the alloys. These changes are convenient for the dehydrogenation of the hydrides and the diffusion of the hydrogen in the alloy.

Figure 6(b) shows the evaluation results of the arranged packing effect of the E5-2 powder (150–1000 μm in size) electrodes. The discharge rate performance of arranged packing electrode was better than that of random packing electrode. The performance of arranged packing electrode was also better than that of arc-melted powder electrode (smaller than 44 μm in size). We confirmed the effect of the packing technique on the improvement of discharge rate performance. As shown in Figure 7, the improvement may be resulted in the shortening effect of the hydrogen diffusion distance in the arranged packing electrode. As reported by Sakai et al.^{7)–11)}, the columnar structure may also assist the hydrogen diffusion in the alloys.

4. Conclusion

We successfully prepared the flaky $\text{LaNi}_{3.5}\text{Co}_{1-x}\text{Cr}_x$

$\text{Al}_{0.1}$ ($x=0, 0.1$) alloy powders by two-stage rapid quenching. The electrodes of the flaky powders had good activation characteristics. The addition of chromium to the flaky alloys led to the improvement of the cyclic durability and the discharge rate performance. Additionally, we confirmed the arranged packing effect of the flaky powders in the disc electrodes on the improvement of the discharge rate performance.

(Received August 1, 2003 ; Accepted November 25, 2003)

References

- 1) J. J. G. Willems ; *Philips J. Res. Report*, 39, 1 (1984)
- 2) H. Ogawa, M. Ikoma, H. Kawano and I. Matsumoto ; *Power Sources*, 12, 393 (1988)
- 3) M. Kanda, M. Yamamoto, K. Kanno, Y. Satoh, H. Hayashiba, and M. Suzuki ; *J. Less-Common Metals*, 172-174, 1227 (1991)
- 4) K. Suzuki, N. Yanagihara, H. Kawano and A. Ohta ; *J. Alloys Compd.*, 192, 173 (1993)
- 5) M. Nogami, M. Tadokoro, M. Kimoto, Y. Chikano, T. Ise and N. Furukawa ; *Denki Kagaku (presently Electrochemistry)*, 61, 1088 (1993)
- 6) C. Iwakura, T. Oura, H. Inoue and M. Matsuoka ; *Electrochim. Acta*, 41, 117 (1996)
- 7) T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa ; *J. Less-Common Metals*, 172-174, 1175 (1991)
- 8) T. Sakai, H. Yoshinaga, H. Miyamura, N. Kuriyama and H. Ishikawa ; *J. Alloys Compd.*, 180, 37 (1992)
- 9) R. Mishima, H. Miyamura, T. Sakai, N. Kuriyama and H. Ishikawa ; *J. Alloys Compd.*, 192, 176 (1993)
- 10) T. Sakai, H. Miyamura, N. Kuriyama, H. Ishikawa, I. Uehara ; *Z. Phys. Chem.*, NF 183, 333 (1994)
- 11) I. Yonezu, A. Furukawa, S. Fujitani, K. Nasako, T. Yonesaki, T. Saito and N. Furukawa ; *Denki Kagaku (presently Electrochemistry)*, 58, 742 (1990)
- 12) F. Meli and L. Schlapbach ; *J. Less-common Metals*, 172-174, 1252 (1991)
- 13) M. Matsuoka, K. Asai, K. Asai, Y. Fukumoto and C. Iwakura ; *J. Alloys Compd.*, 192, 149 (1993)
- 14) S. Kamasaki, H. Soh and Y. Misaki ; *Denki Kagaku (presently Electrochemistry)*, 61, 1445 (1993)
- 15) S. Kamasaki, M. Kihara, Y. Misaki and M. Yamada ; *Journal of The Surface Finishing Society of Japan*, 48, 1237 (1997)
- 16) S. Kamasaki ; *Journal of The Surface Finishing Society of Japan*, 52, 94 (2001)
- 17) J. J. Reilly, G. D. Adzic, J. R. Johnson, T. Vogt, S. Mukerjee and J. Mcbreen ; *J. Alloys Compd.*, 293, 569 (1999)
- 18) M. Oguchi, Y. Harakawa, A. Inoue and T. Masumoto ; *Material Science Eng.*, A 181/A 182, 1161 (1994)
- 19) S. Karashima ; *Kinzoku Data-book*, p. 23 (MARUZEN, 1983)
- 20) Y. Ohsumi ; *Suiso Kyuzou Goukin*, p. 41 (AGNE, 1999)